Phonon scattering by 3d impurities in III-V semiconductors: evidence of a low-spin ground state for V^{2+} in GaAs?

Phonon scattering by 3d impurities in III–V semiconductors: evidence of a low-spin ground state for V²⁺ in GaAs?

N Butler[†], L J Challis[†], M Sahraoui-Tahar[†], B Salce[‡] and W Ulrici[§]

[†] Department of Physics, University of Nottingham, Nottingham NG7 2RD, UK
[‡] CENG, DRFG/SBT/LCP, 85X, 38041 Grenoble Cédex, France
[§] Akademie der Wissenschaften der DDR, Zentralinstitut für Elektronenphysik, 1086 Berlin, German Democratic Republic

Abstract. Phonon scattering by 3d impurities in GaAs, GaP and InP has been investigated by measuring the thermal conductivity between 50 mK and 100 K. Seven of the systems studied conform to the expectation that orbital triplets should scatter more strongly than doublets. It seemed likely that this should also be the case for isolated V²⁺ in GaAs but in fact only weak scattering is observed at high frequencies ($\nu_0 > 100$ GHz). This is interpreted as evidence that V²⁺ in GaAs has a low-spin configuration leading to a doublet ground state, ²E. Two strong phonon resonances are observed at low frequencies, ≈6 and ≈20 GHz. These are sensitive to sub-band-gap illumination and are assigned to a centre previously seen by TDEPR and APR and attributed to a V²⁺ complex.

1. Introduction

Measurements on a number of 3d ions in octahedral coordination indicate that phonon scattering provides a useful signature of the orbital degeneracy of their ground states (see, for example, Challis and de Goër (1984)). Singlets are very weakly coupled and doublets (E) are much more strongly coupled than triplets (T). This can readily be associated with the directions of the lobes of the e and t_2 orbitals with respect to the positions of the ligands. The e lobes point directly towards the ligands so that the potential energy is much more sensitive to the movement of the ligands than in the t_2 case. This argument suggests that, for ions in tetrahedral sites, triplets should be more strongly coupled than doublets, since the orientations of the e and t_2 lobes relative to the ligands are now reversed. Singlets, of course, remain insensitive to phonons. We are presently testing this as part of a detailed study of phonon scattering by 3d ions in GaAs, GaP and InP and have observed a very interesting anomaly for isolated V²⁺ (d³) in GaAs. Scattering from GaAs(V²⁺) at higher frequencies is very much weaker than that in the other T_1 systems which we interpret as evidence that the ground state of V²⁺ has the low-spin state (²E) rather than the expected high-spin (Hund's rule) ⁴T_1 state. A low-spin ground state has never previously been seen in a tetrahedral site of a semiconductor but was recently predicted for V²⁺ in GaAs by Katayama-Yoshida and Zunger (1986) and for V²⁺ in GaAs, GaP and InP by Caldas et al (1986). (Low-spin ground states are
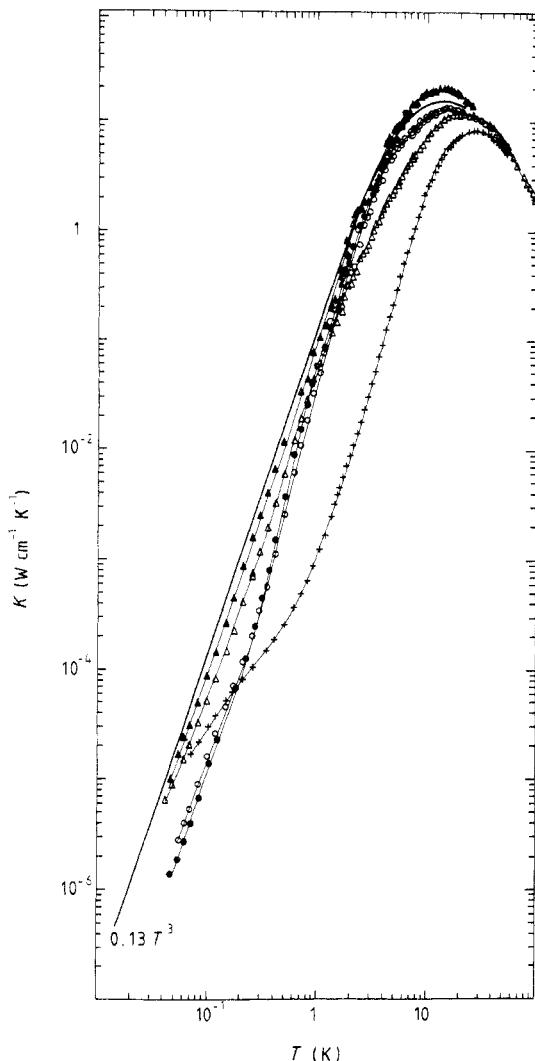
Figure 1. The thermal conductivities of the five samples of V-doped GaAs (▲, 1–1267(2); △, 4–145; ●, CT 798 A; ○, SN 329 A; +, CT 806) together with the data for an undoped specimen of GaAs (GA 803—Challis *et al* 1982).

also extremely rare for transition-metal ions in chemical complexes, with only one example reported to date—Byrne *et al* 1986.)

Undoped samples of GaAs, GaP and InP are normally n-type due to the presence of excess residual shallow donor impurities, particularly Si. 3d impurities (M) usually substitute for Ga or In and so normally enter in the M^{3+} state. However a proportion trap electrons from the shallow donors so that, in nearly all cases, the doped samples contain a mixture of M^{2+} and M^{3+} ions. If the M^{2+}/M^{3+} level lies well away from the band edges, the system can become semi-insulating (SI) with a room-temperature resistance which may approach 10^8 Ω cm (this requires [M] > [shallow donor]). A number of authors have reported semi-insulating GaAs obtained by V-doping (Vasil'ev *et al* 1976, Kaufmann *et al* 1982, Terao *et al* 1982 and Kutt *et al* 1984). The V^{3+} ion has been studied by optical (Clerjaud 1985, and references therein) and EPR measurements (Kaufmann *et al* 1982) and identified as having a ground-state singlet ($^3A_2$) as expected.

Table 1. Sample characteristics—please note the slight differences between this table and that in Butler *et al* (1987) which are referred to, in detail, in the caption to table 2.

Sample	Reference Nos	Source	Length (mm)	Cross section (mm)^2	Long axis	Carrier type (300 K)	Resistivity (Ω cm) (300 K)
GaAs	GA 803	4	16	3.10×3.40	$\langle 110 \rangle$	n	NA
GaAs:V	1–1267 (2)	1	11	4.38×4.53	$\langle 110 \rangle$	SI	5×10^6
	4–145	1	7.5	3.18×3.02	$\langle 110 \rangle$	SI	2×10^6
	CT 798 A	2	7.8	3.41×2.64	$\langle 110 \rangle$	n	1
GaAs:V:Si	SN 329 A	2	18	2.78×2.93	$\langle 111 \rangle$	n	0.05
GaAs:V:Zn	CT 806	2	14	1.91×3.35	$\langle 110 \rangle$	p	0.8
GaAs:Ni	TN 593 E	2	18	2.98×2.96	$\langle 100 \rangle$	p	60
GaAs:Cr	TI4	3	18	3.00×5.00	$\langle 100 \rangle$	SI	NA
	GA 735 (e)	4	15	2.90×3.00	$\langle 110 \rangle$	SI	NA
GaAs:Ti	Boule II A1	2	16	2.85×2.87	$\langle 110 \rangle$	n	0.3
GaP:V	E1	2	15	3.38×3.19	$\langle 110 \rangle$	SI	3×10^8
GaP:Cr	MCP1 c	5	15	1.64×3.34	$\langle 110 \rangle$	SI	NA
InP:Cr	S 39	6	17	5.25×0.34	$\langle 110 \rangle$	SI	NA
InP:Fe	1033/R4	7	19	3.18×4.53	$\langle 110 \rangle$	SI	8×10^5

NA: Not available.
Sources: 1, Wacker Chemitronic; 2, Zentralinstitut für Elektronenphysik, Berlin; 3, Sumitomo Co; 4, Plessey Co; 5, MCP Ltd; 6, RSRE, Malvern; 7, Cambridge Instruments Ltd.

Much less is known about V^{2+}. The V^{2+}/V^{3+} level is widely believed to lie 0.14 eV below the conduction band edge (E_c) and the V^{3+}/V^{4+} level to lie close to the valence band edge (Brandt *et al* 1985, Clerjaud *et al* 1985 and Ulrici *et al* 1985).

A V-related level at about 0.23 eV below the conduction band has also been reported by several groups of workers (Haisty and Cronin 1964, Litty *et al* 1983, Clerjaud *et al* 1985) and is often attributed to a complex of V with an unknown defect (see for example Ulrici *et al* 1985, 1987). Such complexes have been invoked by a number of authors to explain a wide variety of measurements (for example: TDEPR, Vasson *et al* (1984) and En-Naqadi *et al* (1988); optical absorption and luminescence, conventional EPR and temperature-dependent Hall effect, Ulrici *et al* (1985, 1987); APR Rampton *et al* (1986); and acoustic attenuation, Atkinson and King (1987)). Indeed it now seems likely that two such complexes have been detected (Ulrici *et al* 1987) labelled (V–X) and V^{2+} (II). The former is observed in optical and conventional EPR measurements and the latter by TDEPR and APR. The evidence for two centres comes from a consideration of the effects of illuminating the samples with sub-band-gap radiation. After irradiation, with $h\nu > 1.05$ eV, signals are created (or enhanced) in optical and EPR experiments which decay at low temperatures with a lifetime of about three hours. (This decay can be greatly accelerated by illumination with $h\nu < 1.0$ eV.) Radiation also creates or enhances TDEPR and APR signals but in this case the effective frequency range is 0.7 eV $< h\nu < 1.5$ eV and the centres created are stable, with low-temperature lifetimes $\geq$ days. In samples which are weakly n-type at room temperature, small signals seen in the dark are greatly enhanced by illumination while SI samples only display signals after illumination.

The effects of illumination on acoustic attenuation have also been studied. The results seem closest to the conventional EPR and optical experiments although the decay observed is considerably faster. This work is discussed further in § 3.

2. Results

2.1. The thermal conductivity of GaAs(V)

Figure 1 shows the thermal conductivity (K) of five samples of GaAs(V) and one of undoped GaAs. One of the GaAs(V) samples is co-doped with Si and another with Zn: the sample characteristics are listed in tables 1 and 2. It is seen that, for four samples, the V doping has at most only a modest effect on the conductivity about 1 K but more pronounced effects are apparent below this temperature. The conductivity of the fifth sample (CT 806) co-doped with Zn, lies well below that of the others and we attribute this to scattering by the localised holes at the Zn sites (Holland 1964, Carlson *et al* 1965 and Jouglar and Vuillermoz 1982). This sample, therefore, will not be discussed further. It is convenient to consider the scattering by V ions in GaAs in two frequency ranges and compare it with that of several other systems.

2.2. High-frequency scattering (>100 GHz)

Figure 2 shows the thermal resistivity ($W = 1/K$) data of representative samples of the different systems between 4 and 20 K. The results are plotted in the reduced form W/W_0, where W_0 is the resistivity of the undoped host material; a curve for GaP(Cr) is omitted as the higher concentration of Cr (4×10^{17} cm$^{-3} \simeq 8$ PPM) present in the sample measured leads to a reduced resistivity $W/W_0 \simeq 200$, too large for the figure. Because of the conduction band structure of GaP (indirect gap) strong resonant phonon scattering is produced by the traces of shallow donors always present in undoped material (Butler *et al* 1985, 1986b). We have therefore had to estimate W_0 for GaP by using values for GaAs adjusted to join, below 4 K, those calculated for GaP assuming only boundary scattering. The W/W_0 curves fall into two groups: an upper one, with $W/W_0 > 10$, which contains GaAs(Cr), InP(Cr), GaP(Cr), GaP(V) and GaAs(Ni) and a lower group, $W/W_0 < 3$, that consists of InP(Fe), GaAs(Ti) and GaAs(V). W/W_0 is determined by the product of the concentration and the cross section of the scattering centres but if, for the moment, we assume the concentrations to be comparable, the data imply that the cross sections of the first five systems in this frequency range are substantially greater than those of the latter three.

    The impurity concentrations shown in table 2 were obtained by SIMS analysis (Loughborough Consultants Ltd). The last but one column shows the ground state of the M^{2+} or M^{3+} ion thought to be responsible for most of the scattering, the active ion. The alternative ions have orbital singlet ground states, except in the case of Cr, and so are relatively weakly coupled. The exception, Cr^{2+}, has an orbital triplet ground state ($^5T_2$) but this only scatters at very low frequencies and is not thought to contribute significantly to the thermal resistance above 0.5 K (Challis *et al* 1982). It is seen, then, that the active ions in the five systems showing the strongest scattering at these frequencies all have orbital triplet ground states and that two of the active ions showing weaker scattering have orbital doublet ground states and so conform with the proposal made earlier. We note, however, the exception of V^{2+} in GaAs. According to Hund's rule this should have a $^4T_1$ ground state but the strength of the high-frequency scattering is evidently very different from that of V^{2+} in GaP, Cr^{3+} in GaAs, GaP and InP and Ni^{2+} in GaAs and seems more characteristic of samples doped with ions in E states. The scattering is greatest at around 7 K which corresponds approximately to a resonant scattering frequency of 600 GHz (the dominant phonon frequency about $80T$ GHz). This is very

Table 2. Sample characteristics—impurity concentrations of samples as determined by SIMS or spectrochemical analysis. The penultimate column shows the isolated impurity valence state expected to contribute most significantly to the phonon scattering (active ion). An estimate of the concentration of this centre is made from the SIMS or spectrochemical analysis data for the impurity in question and from optical and electrical measurements; the figure for Ni in CT 798 A given in a preliminary report (Butler *et al* 1987) is in error. No value is quoted here because the SIMS technique is insensitive to this species at concentrations less than $\approx 10^{16}$ cm^{-3}. We note the relatively high concentrations of trace impurities—such as Cr, Mn and Fe—found in material grown by Wacker-Chemitronic. These ions might well influence the electrical, as well as the phonon scattering, characteristics of the samples with two important consequences: (i) preferential trapping of electrons by these other centres could lead to lower concentrations of V^{2+}, in the Wacker-Chemitronic specimens, than quoted in this table; (ii) such a proposal could explain the high-room-temperature resistivities of these crystals, in comparison with most other GaAs:V material; see discussion. (We note that in Butler *et al* 1987 there are some discrepancies with this table. The GaP(V) sample is SI and the GaAs(Ti) sample n-type while the [Ni] for CT 798 A is in error. The rest of the information given in that table is correct, but further information has now been added.)

| Sample	Ref Nos	[Ti] (cm^{-3})	[V] (cm^{-3})	[Cr] (cm^{-3})	[Mn] (cm^{-3})	[Fe] (cm^{-3})	[Ni] (cm^{-3})	Active ion	Estimated concentration of active ion (10^{16} cm^{-3})
GaAs	GA 803	NA	NA	NA	NA	NA	NA	—	—
GaAs:V	1–1267(2)	NA	3×10^{16}	6×10^{15}	$\leqslant 10^{15}$	3×10^{16}	NA	V^{2+}(^{2}E or ^{4}T$_1$)	≈ 0
GaAs:V	4–145	NA	2×10^{17}	1×10^{17}	2×10^{16}	NA	NA	V^{2+}(^{2}E or ^{4}T$_1$)	≈ 0
GaAs:V	CT 798 A	$\leqslant 10^{14}$	5×10^{16}	$\leqslant 10^{14}$	$\leqslant 10^{14}$	$\leqslant 10^{14}$	NA	V^{2+}(^{2}E or ^{4}T$_1$)	≈ 2–4
GaAs:V:Si	SN 329 A	NA	4×10^{16}	8×10^{14}	$\sim 1 \times 10^{15}$	NA	NA	V^{2+}(^{2}E or ^{4}T$_1$)	≈ 4
GaAs:V:Zn	CT 806	NA	3×10^{16}	NA	NA	NA	NA	see text	
GaAs:Ni	TN 593 E	NA	NA	2×10^{14}	2×10^{15}	NA	-2×10^{17}	Ni^{2+}(^{3}T$_1$)	≈ 2.5
GaAs:Cr	TI4	NA	NA	6×10^{15}	$\leqslant 10^{15}$	NA	NA	Cr^{3+}(^{4}T$_1$)	$\leqslant 0.6$
GaAs:Cr	GA 735(e)	NA	NA	2×10^{17}	NA	NA	NA	Cr^{3+}(^{4}T$_1$)	$\leqslant 20$
GaAs:Ti	Boule II A1	2×10^{16}	5×10^{15}	6×10^{14}	$\leqslant 10^{15}$	NA	NA	Ti^{3+}(^{2}E)	<2
GaP:V	—	NA	4×10^{16}	4×10^{17}	NA	NA	NA	V^{2+}(^{4}T$_1$)	<4
GaP:Cr	MCP1 c	NA	NA	4×10^{17}	NA	NA	NA	Cr^{3+}(^{4}T$_1$)	≈ 40
InP:Cr	S 39	NA	NA	NA	NA	NA	NA	Cr^{3+}(^{4}T$_1$)	NA
InP:Fe	1033/R4	NA	NA	8×10^{14}	2×10^{14}	2×10^{17}	NA	Fe^{2+}(^{2}E)	~ 20

NA: Not available.

v (GHz)
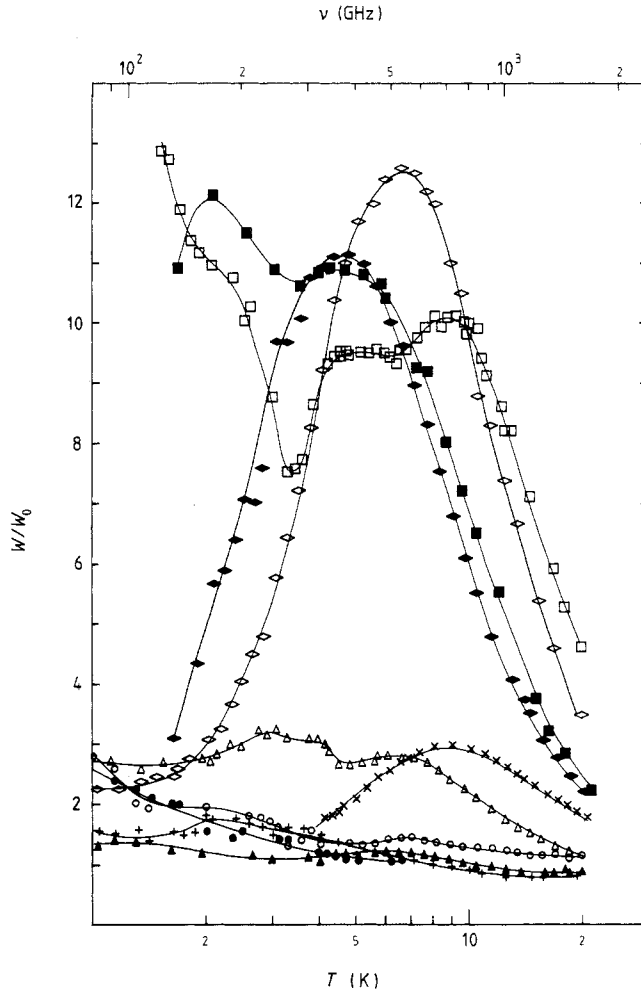
Figure 2. The reduced thermal resistivity (W/W_0) as a function of temperature, for the samples described in tables 1 and 2 (GaAs(V): ▲, 1–1267(2); △, 4–145; ●, CT 798 A; ○, SN 329 A; GaAs(Ni): ◆, TN 593 E; GaAs(Cr): □, GA 735(e); +, GaAs(Ti); ◇, GaP(V); ■, InP(Cr) 539; ×, InP(Fe) 1033/R4). There are slight differences between these curves and those shown in Butler *et al* 1987. W_0 for the GaP(V) sample is discussed in the text. The curve for the GaP(Cr) sample is omitted because of the large values of W/W_0 (≈150–200). The frequency scale marked above the figure, and above figures 3, 4 and 5 is obtained assuming the dominant phonon approximation ($h\nu = 3.8\,kT$) and is a rough guide to the resonance frequencies.

similar to the frequency inferred from acoustic relaxation measurements on CT 798 A by Atkinson and King (1987).

2.3. Low-frequency scattering (<100 GHz)

Figure 3 shows the reduced resistivity of the GaAs(V) samples down to 50 mK. Strong resonant scattering is apparent in two of the samples corresponding to frequencies ≈6 and ≈20 GHz. The strong scattering occurs in the samples with the Fermi level either at
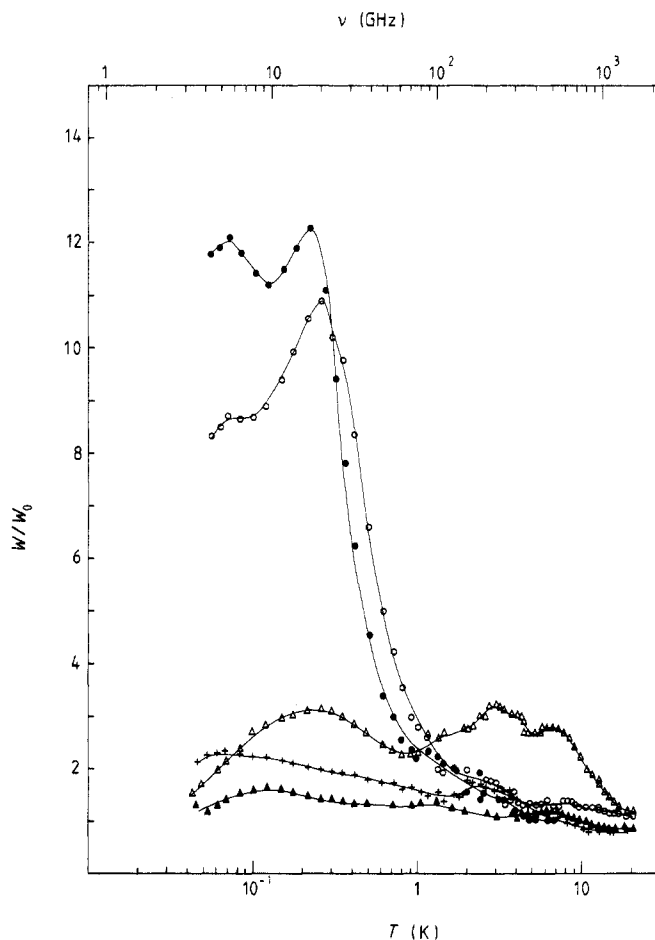
Figure 3. The reduced thermal resistivity (W/W_0) of the GaAs(V) samples at low temperatures (▲, 1-1267(2); △, 4–145; ●, CT 798 A; ○, SN 329 A). Included, for comparison, are data for the GaAs(Ti) specimen (+) which may contain some Ti^{3+}, an ion expected to have a ^2E ground state.

the V^{2+}/V^{3+} level, $E_c - 0.14$ eV (sample CT 798 A) or near the conduction band edge (sample SN 329 A) but is absent in the samples 1-1267(2) and 4–145, where the Fermi level is near the midgap (see table 1). The positions of the Fermi-levels were inferred from optical and electrical measurements.

2.4. Effects of illumination

The thermal conductivities of the samples were also measured after illumination with an infrared diode of the same type used in both the APR and TDEPR experiments. The diode emitted a broad band of radiation centred at 930 nm (1.33 eV) and was placed about 2–3 mm away from the specimen. Illumination was typically for 2–3 s, the diode passing a current of 15 mA with a potential difference across the electrodes of 30–35 V.
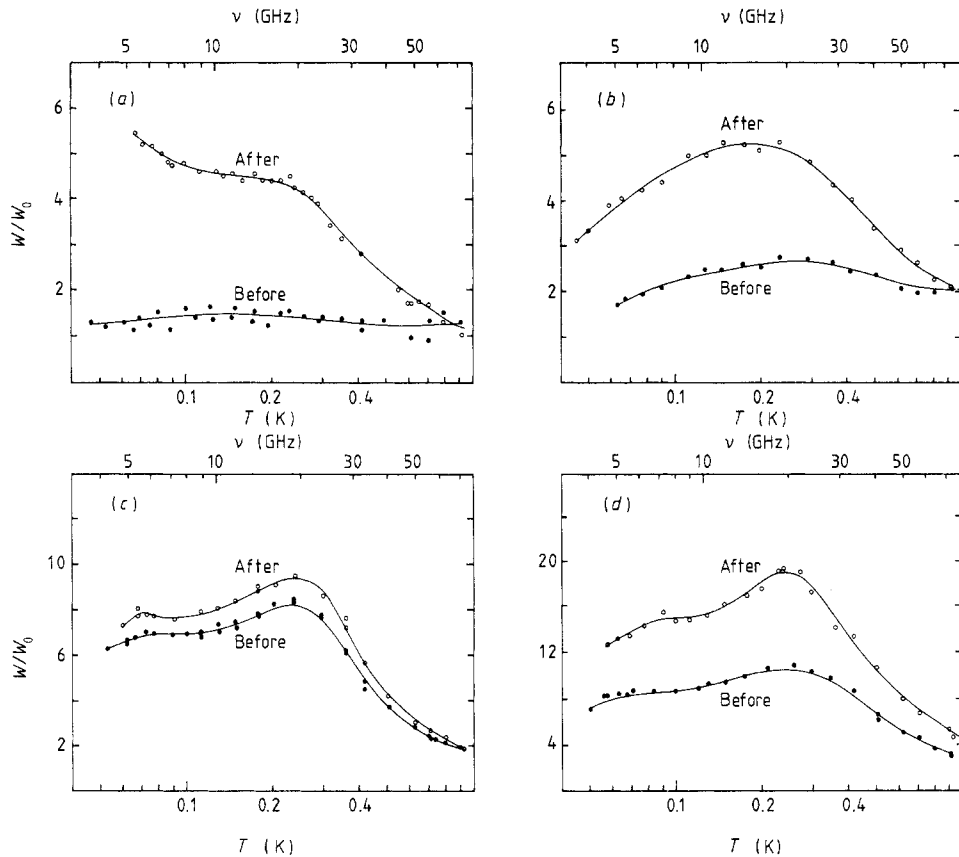
Figure 4. The reduced thermal resistivity of the four GaAs(V) samples before (●) and after illumination (○) with an infrared diode. The samples shown in (*a*) and (*b*) are semi-insulating and those in (*c*) and (*d*) are n-type. (*a*), 1–1267(2); (*b*) 4–145; (*c*, CT 798 A; (*d*), SN 329 A.

Above 1 K it was possible to investigate the frequency dependence using an optic fibre pipe coupled to a monochromator with a halogen projector bulb as a light source. The long wavelength cut-off of the fibre was about 0.78 eV and we assume that, for the sample dimensions involved (see table 1), radiation of frequency greater than the band gap does not penetrate the crystal sufficiently deeply to affect the vast majority of the impurity states in the bulk. The effective frequency range therefore was about 0.78 eV < $h\nu$ < 1.5 eV. For experiments below 1 K, made in a ^{3}He/^{4}He dilution refrigerator, the introduction of the optic fibre posed technical difficulties which have yet to be resolved, consequently illumination was restricted to the diode.

No detectable changes in the thermal conductivity were apparent above 1 K after illumination with either the diode or the optic fibre. Figure 4, however shows the thermal resistivities below 1 K of the four n-type or SI samples, both before and after illumination. It is seen that in the two SI samples (figures 4(*a*) and (*b*)) strong phonon scattering is created by the radiation which can, in the case of 1–1267(2), be resolved into two peaks centred at about 6 and 20 GHz, in good agreement with those seen in the n-type specimens in the dark. For the n-type crystals (figures 4(c) and (d)) the phonon scattering observed in the dark is enhanced by illumination. The additional scattering created can
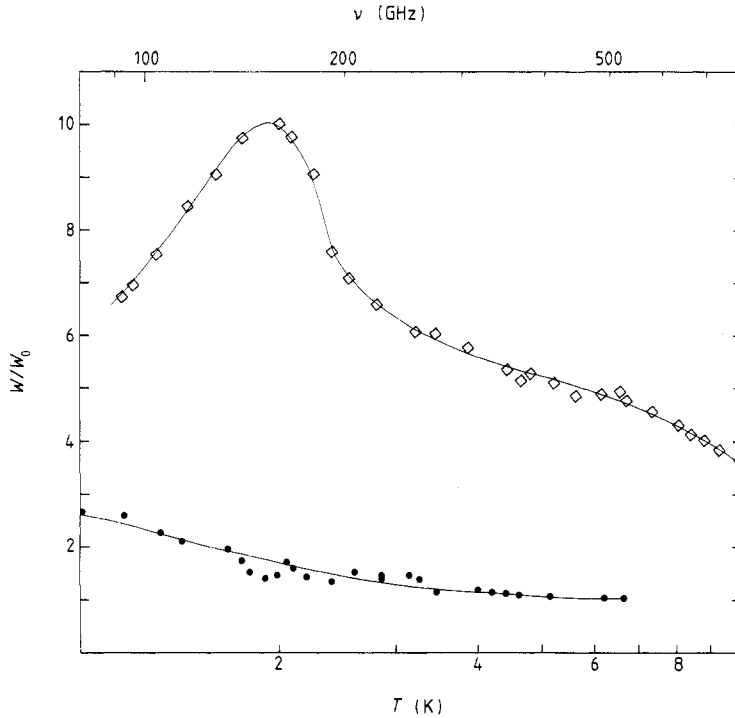
v (GHz)

Figure 5. A detailed comparison of the reduced thermal resistivity for the samples CT 798 A (GaAs : V) (full circles) and TI4 (GaAs : Cr) (open diamonds). There are slight differences between these curves and those shown in Butler *et al* 1987. (These differences are the result of more recent improved measurements on the undoped GaAs reference sample, GA 803.)

be completely removed by thermally annealing the samples at room temperature but is persistent, on a timescale of at least several days, if the specimens are kept at 4 K.

The data shown in figure 4 were taken about one year after those that appear in figure 3. It can be seen that significant changes in W/W_0 in the dark have occurred for one of the n-type samples (CT 798 A); the same specimen was used in each case and the thermometer contacts were not removed between the two sets of experiments. Possible reasons for the change are considered below.

3. Discussion

3.1. Phonon scattering above 100 GHz

From figure 2 and table 2 it is evident that all samples which contain impurities with a $^4T_1$ or a $^3T_1$ ground state, with the exception of $GaAs(V^{2+})$, exhibit strong phonon scattering in the high-frequency region (>100 GHz). The anomalous behaviour of $GaAs(V^{2+})$ is seen in the drastic difference between the phonon scattering of the isoelectronic systems $GaAs(V^{2+})$ and $GaAs(Cr^{3+})$. This is further illustrated in figure 5 which compares W/W_0 for two GaAs samples. The concentration of V^{2+} is greater by a factor of about 2 or more than that of the Cr^{3+} but the scattering is very much weaker in this frequency range.

In analysing the behaviour of the GaAs(V) samples investigated we have to take into account the following. The samples 1–1267(2) and 4–145 show high resistivity at 300 K so that the V^{2+}/V^{3+} level at $E_c - 0.14$ eV is always empty, i.e. there are no V^{2+} ions in the samples. On the other hand, it has been proved by optical and electrical measurements that in CT 798A the V^{2+}/V^{3+} level is partly filled and that in SN 329A all isolated V is in the V^{2+} state (Fermi level near the conduction band edge). It is clear that there is no correlation between the scattering at approximately 7 K and the V^{2+} concentration. The scattering is greatest in 4–145 which contains no V^{2+} and very much weaker in SN 329A and CT 798A which probably contain the most. Further evidence that V^{2+} does not scatter above 100 GHz comes from the illumination experiments: no enhancement of the scattering could be detected for $T > 1$ K although the optically induced recharging experiments (Ulrici *et al* 1987) clearly indicate an increase of $[V^{2+}]$ under illumination. We conclude that the scattering at approximately 7 K is caused by other ions present as trace impurities and that V^{2+} in GaAs does not scatter phonons significantly in this frequency range.

In the SI and weakly n-type samples the trace impurities responsible for the scattering seem likely to be Ni^{2+} and/or Cr^{3+}. The data for GaAs(Ni) can be very well described by a single resonant process at 300 GHz due to Ni^{2+} (Sahraoui-Tahar *et al* 1988) and we have computed that a maximum value $W/W_0 = 2$ is produced by a Ni^{2+} concentration of about 1.5×10^{-2} of that in TN 593E, that is about 4×10^{14} cm^{-3}. A still smaller concentration of Cr^{3+} would be needed since this is even more strongly coupled to phonons than Ni^{2+}. We note the very high concentrations of Ni and Cr present in sample 4–145 (table 2) which shows the strongest scattering in this frequency range. For Cr at least, this concentration seems improbably high since comparison of the W/W_0 values in figure 2 with values for GaAs(Cr), (Challis *et al* 1982) suggest that $[Cr^{3+}] < 1 \times 10^{15}$ cm^{-3} with perhaps a similar limit for $[Cr^{2+}]$. However, since the Cr^{2+}/Cr^{3+} level lies below that of V^{2+}/V^{3+}, we cannot rule out the possibility that most of the Cr is in the Cr^{2+} state and that the low-frequency scattering from this is quenched by strain.

The source of the scattering in the more heavily n-type GaAs(V) samples CT 798A and SN 329A is less clear. The Cr and Ni ions will now be in their Cr^{2+} and Ni^{1+} states neither of which gives rise to phonon scattering at these frequencies. This, however, assumes homogeneity in the samples which in practice may include small regions with different electrical characteristics containing some Cr^{3+} and Ni^{2+}; only traces would be required to account for the very weak scattering observed—similar arguments may be found in Butler *et al* 1986a. We conclude that the scattering at about 7 K is probably caused by trace impurities and that these, rather than V^{2+}, are responsible for the acoustic attenuation seen by Atkinson and King (1987). We note that they assigned this attentuation to V^{2+} and from evidence that it is sensitive to T_2 symmetry distortions concluded that V^{2+} has a T_1 ground state.

3.2. Phonon scattering below 100 GHz

The resonances in the phonon scattering at approximately 6 and 20 GHz are in good agreement with two of the transition frequencies, 4.0 and 17.6 GHz, between the three Kramers doublets ($J = \frac{3}{2}$) deduced from the analysis of the TDEPR spectrum seen in the same samples (En-Naqadi *et al* 1988). (We believe the frequency of the third splitting, at $\simeq 14$ GHz, is too close to 20 GHz for us to resolve.) It is also known from APR that the centre responsible is strongly coupled to phonons. These phonon resonances are absent in the samples 1–1267(2) and 4–145 in the dark but appear after illumination with sub-

band-gap light showing exactly the same behaviour seen in the TDEPR and APR resonances and we conclude that this low-frequency phonon scattering is from the centre responsible for the TDEPR and the APR.

The analysis of the TDEPR spectrum (En-Naqadi *et al* 1988) is consistent with a $^4T_1$ ion, presumably either isolated V^{2+} or a V^{2+} complex. However, both the TDEPR and APR spectra are assigned to V^{2+}complexes, labelled V^{2+}(II) because the photo-induced effects seen in these experiments differ in two important aspects from those seen in the optical measurements of isolated V^{2+} by Ulrici *et al* (1987). Firstly the optical signal of isolated V^{2+} decays significantly over a period of a few hours after the illumination is switched off while little or no decay is seen after the illumination is stopped in the case of TDEPR or APR. Secondly the optical frequency dependence of the effects in TDEPR and APR differs from that of the optical studies of isolated V^{2+} (see also § 1). It should be noted, however, that the measured decay of the optical signal from isolated V^{2+} is logarithmic. In a model of logarithmic decay (e.g., Queisser and Theodorou (1986)) it is the number of ions that decays as $-\ln(t/\tau)$, not the fraction. Therefore a high initial concentration will take longer to decay to one half of its original value, say, than a small concentration. Hence it could be argued that the larger time of decay in the TDEPR and APR experiments is a consequence of a higher photo-induced concentration. We believe this is not true, however, since the optical measurements suggest that a high proportion of the available centres is changed by the illumination, so the concentration of the photo-induced centres must be at least comparable with, if not higher than, those produced in the TDEPR and APR experiments.

Because of the similarities between our present results and those of TDEPR and APR experiments we attribute the low-frequency phonon scattering to V^{2+}(II) complexes. The strength of the scattering may indicate that the concentration of the complex is quite high and it would be of interest to have further information on this. It does not seem possible to measure the concentration of the complex by DLTS, however, since experiments on SN 329A, which appears from this work to contain the highest concentration in our samples, shows only one level at $E_c - 0.14\,eV$ (Bremond *et al* 1989). It seems highly unlikely that the complex concentration is too small to detect so presumably this indicates that the V^{2+}(II)/V^{3+}(II) and V^{2+}/V^{3+} levels are too close to resolve.

Finally we note that the decrease in the thermal resistivity below 1 K of one of the n-type samples, in an experiment made a year later than the first (both measurements were made in the dark), suggests that the concentration of the V^{2+}(II) centre in this specimen has decayed with time. It is possible that this effect can be understood in terms of the following model. When the crystal is formed the concentration of defects and so of V^{2+}(II) centres is higher than the thermal equilibrium distribution. The concentration of V^{2+}(II) falls as a result of the slow decay, at room temperature, of the concentration of the associated defect.

4. Conclusion

The ground state of V^{2+} in GaAs is clearly very different from that of Cr^{3+} in GaAs, GaP and InP, Ni^{2+} in GaAs and V^{2+} in GaP. The very weak scattering at frequencies >100 GHz is in marked contrast with the strong scattering seen in other d^3 and d^8 systems. We suggest this is evidence that the ground state is a low-spin ^2E (see also Butler *et al* 1987). This interpretation is supported by the recently published results of MCD–ODMR investigations on GaAs(V^{2+}) indicating that the ground state of V^{2+} has a spin of

$\frac{1}{2}$ (Görger *et al* 1988). We cannot however rule out the possibility that it is a $^4T_1$ state undergoing a tetragonal dynamic Jahn–Teller distortion with tunnelling frequencies, $\ll 5$ GHz in analogy with GaAs (Cr^{2+}); $^5T_2$ (Challis *et al* 1982), although it would seem surprising that the $^4T_1$ state should behave so very differently in this case. The strong scattering at about 6 and 20 GHz is attributable to the $V^{2+}(II)$ complex centre seen in TDEPR and APR, which has a $^4T_1$ ground state (En-Naqadi *et al* 1988). Presumably in the isolated V^{2+} ion, the $^4T_1$ level is an excited state lying just above the ^2E (Katayama-Yoshida and Zunger 1986, Caldas *et al* 1986) and the proximity of the defect forming the complex lowers the energy of the $^4T_1$ state, relative to that of the ^2E, such that the $^4T_1$ now becomes the ground state. Weak scattering in GaAs(V) seen at approximately 600 GHz is attributable to traces of Ni^{2+} or Cr^{3+}. The strong high-frequency phonon scattering from SI GaP(V) suggests that V^{2+} has a $^4T_1$ ground state in GaP and not a low-spin ground state as predicted by Caldas *et al* (1986). This will be the subject of a future publication and has also been described in a recent conference report (Butler *et al* 1988).

Acknowledgments

References

Atkinson I and King P J 1987 *J. Phys. C: Solid State Phys.* **20** 2069–80
Brandt C D, Hennel A M, Pawlowicz L M, Dabkowski F P, Lagowski J and Gatos H C 1985 *Appl. Phys. Lett.* **47** 607–9
Bremond G, Hizen N, Guillot G, Gavand N, Nouailhat A and Ulrici W 1989 *J. Electron. Mater.* submitted
Butler N, Challis L J and Cockayne B 1986a *Proc. 5th Int. Conf. Phonon Scattering in Condensed Matter (Urbana, IL) 1986* ed. A C Anderson and J P Wolfe (Berlin: Springer) pp 144–6
Butler N, Challis L J, Sahraoui-Tahar M, Salce B and Ulrici W 1987 *Japanese J. Appl. Phys.* **26** Suppl. 26-3 675–6
—— 1988 unpublished
Butler N, Challis L J, Sahraoui-Tahar M, Salce B, Ulrici W and Cockayne B 1988 *Proc. 15th Int. Conf. Defects in Semiconductors (Budapest)* at press
Butler N, Jouglar J, Salce B, Challis L J, Ramdane A and Vuillermoz P L 1986b *Proc. 5th Int. Conf. Phonon Scattering in Condensed Matter (Urbana, IL) 1986* ed. A C Anderson and J P Wolfe (Berlin: Springer) pp 123–5
Butler N, Jouglar J, Salce B, Challis L J and Vuillermoz P L 1985 *J. Phys. C: Solid State Phys.* **18** L725–30
Byrne E K, Richeson D S and Theopold K H 1986 *J. Chem. Soc. Chem. Commun.* 1491–2.
Caldas M J, Figueiredo S K and Fazzio A 1986 *Phys. Rev.* B **33** 7102–9
Carlson R O, Slack G A and Silverman S J 1965 *J. Appl. Phys.* **36** 505–7
Challis L J and de Goër A M 1984 *The Dynamical Jahn–Teller Effect in Localized Systems* ed. Yu E Perlin and M Wagner (Amsterdam: North-Holland) pp 533–708
Challis L J, Locatelli M, Ramdane A and Salce B 1982 *J. Phys. C: Solid State Phys.* **15** 1491–32
Clerjaud B 1985 *J. Phys. C: Solid State Phys.* **18** 3615–61
Clerjaiud B, Naud C, Deveaud B, Lambert B, Plot B, Bremond G, Benjeddou C, Guillot G and Nouailhat A 1985 *J. Appl. Phys.* **58** 4207–15

En-Naqadi M, Vasson A, Vasson A-M, Bates C A and Labadz A F 1988 *J. Phys. C: Solid State Phys.* **21** 1137–53

Görger A, Meyer B K, Spaeth J-M and Hennel A M 1988 *Semicond. Sci. Technol.* **3** 832–8

Haisty R W and Cronin G R 1964 *Physics of Semiconductors* ed. M Hulin (Paris: Dunod) pp 1161–7

Holland M G 1964 *Physics of Semiconductors* ed. M Hulin (Paris: Dunod) pp 713–7

Jouglar J and Vuillermoz P L 1982 private communication

Katayama-Yoshida H and Zunger A 1986 *Phys. Rev.* B **33** 2961–4

Kaufmann U, Ennen H, Schneider J, Worner R, Weber J and Kohl F 1982 *Phys. Rev.* B **25** 5598–605

Kutt W, Bimberg D, Maier M, Krautle H, Kohl F and Bauser E 1984 *Appl. Phys. Lett.* **44** 1078–80

Litty F, Leyral P, Loualiche S, Nouailhat A, Guillot G and Lannoo M 1983 *Physica* B **117/118** 182–4

Queisser H J and Theodorou D E 1986 *Phys. Rev.* B **33** 4027–33

Rampton V W, Saker M K and Ulrici W 1986 *J. Phys. C: Solid State Phys.* **19** 1037–43

Sahraoui-Tahar M, Butler N, Challis L J, Salce B and Ulrici W 1988 *Proc. 19th Int. Conf. Physics of Semiconductors (Warsaw)* at press

Terao H, Sunakawa H, Ohata K and Watanabe H 1982 *Semi-insulating III–V Materials (Evian) 1982* ed. S Makram-Ebeid and B Tuck (Nantwich: Shiva) pp 54–60

Ulrici W, Friedland K, Eaves L and Halliday D P 1985 *Phys. Status Solidi* b **131** 719–28

Ulrici W, Kreissl J, Vasson A, Vasson A-M and En-Naqadi M 1987 *Phys. Status Solidi* b **143** 195–206

Vasil'ev A V, Ippolitova G K, Omel'yanovskii E M and Ryskin A I 1976 *Fiz. Tekh. Polyprovdn.* **10** 571–3 (Engl. Transl. 1976 *Sov. Phys.–Semicond.* **10** 341–2)

Vasson A-M, Vasson A, Bates C A and Labadz A F 1984 *J. Phys. C: Solid State Phys.* **17** L837–41